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A coupled-cluster study of the enthalpy of formation of nitrogen sulfide, NS

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Abstract

The energy of NS was computed via CCSD(T) theory, together with extrapolation to the complete basis set limit and corrections for anharmonic zero-point energy, scalar and vector relativistic terms, and core–valence electron correlation. The results were employed with three working reactions to find $\Delta_f H_0(\mathrm{NS}) = 277.3 \pm 2$ kJ mol^{-1} and $\Delta_f H_{298}(\mathrm{NS}) = 278.0 \pm 2$ kJ mol^{-1}. This thermochemistry is consistent with, but much more precise than, earlier literature values.

1. Introduction

Depending on the conditions, sulfur in flames has been found to enhance or suppress formation of nitrogen oxides [1–8]. The mechanism(s) are unknown. A species which couples nitrogen and sulfur chemistry is nitrogen sulfide, NS. This molecule has been detected in sulfur-seeded flames [9], and there have been studies of some of its reaction kinetics by Blitz and Pilling [10]. The spectroscopy of NS is known in some detail [11], but its thermochemistry is highly uncertain. O'Hare [12] used spectroscopic data to obtain $\Delta_f H_0(\mathrm{NS}) = 281 \pm 24$ kJ mol^{-1}, while two critical evaluations recommend 263 ± 50 and 267 ± 105 kJ mol^{-1} for this quantity, respectively [13,14]. An MRD-CI computational study of a number of electronic states of NS by Lie et al. [15] implied $\Delta_f H_0(\mathrm{NS}) = 351$ kJ mol^{-1}, while more recent computational work by Nguyen et al. [16], involving calculation of H_2NSH and HNS thermochemistry, yielded 282 ± 13 kJ mol^{-1}. The aim of the present work is to apply high accuracy coupled-cluster theory [17–19] to this problem, to establish a reliable value of $\Delta_f H(\mathrm{NS})$ for use in flame modeling.

2. Methodology

Our approach is similar to the one we employed to investigate the thermochemistry of H_2S and SH [20]. Briefly, UCCSD(T)/RHF energies were computed with the MOLPRO program [21] using a series of correlation consistent basis sets of up to quintuple zeta quality. Geometries and energies of NS and other species were obtained with the basis

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sets aug-cc-pVDZ through aug-cc-PV5Z [22,23] and the same geometries were employed with the aug-cc-pV(n + d)Z basis [24], where +d refers to the addition of inner polarization functions and n ran from 2 to 5. Core electrons were excluded from the correlation treatment. CCSD(T) core–valence correlation corrections were obtained with the cc-pwCVQZ basis set of Peterson [25] employed at the geometries optimized at the CCSD(T)/aug-cc-pV5Z level. Vector relativistic corrections to the CCSD(T) energy were derived from experimental spin–orbit splittings [11,14]. Scalar relativistic corrections were derived from CISD/aug-cc-pV5Z calculations as the sum of mass–velocity and Darwin terms [26]. Experimental harmonic frequencies ω_e and anharmonic terms $x_e\omega_e$ were used to derive zero-point vibrational energy corrections [11,20]. In principle, a further small contribution 'E_0' to the zero-point energy arises from third and fourth derivatives of the molecular potential energy [27]. We investigated this for NS at the CCSD(T)/aug-cc-pVTZ level over ±0.1 Å around the equilibrium geometry, and found E_0 to be less than 0.2 kJ mol^{-1}. Depending on the force field used, E_0 lies between 0–0.25 kJ mol^{-1} for the H_2O molecule [28]. Accordingly, we do not consider these higher-order effects further.

These data were used in three working reactions to obtain the thermochemistry of NS:

$$NS \rightarrow N + S \quad (1)$$

$$NS + H_2O \rightarrow NO + H_2S \quad (2)$$

$$NS + O_2 \rightarrow NO + SO \quad (3)$$

The computed 0 K reaction enthalpies of each process were combined with experimental heats of formation of the other species to find $\Delta_f H_0$(NS).

3. Results and discussion

Table 1 summarizes the geometry of NS obtained with different basis sets. It may be seen that the error at the highest level of theory is only 0.003 Å. An exponential extrapolation to the complete basis set (CBS) limit, i.e., to $n = \infty$ in the aug-cc-pVnZ series, yields $r_e = 1.4938$ Å which is essentially equal to the experimental value [11]. A Morse potential fit to the CCSD(T)/aug-cc-pVTZ data for NS yields values of $\omega_e = 1204$ cm^{-1} and $\omega_e x_e = 6.8$ cm^{-1}, which are in good accord with the experimental values employed here of 1219 and 7.3 cm^{-1}, respectively [11].

Table 1
Geometry of NS

Method	N–S bond length, r_e (Å)
CCSD(T)/aug-cc-pVDZ	1.5379
CCSD(T)/aug-cc-pVTZ	1.5129
CCSD(T)/aug-cc-pVQZ	1.5030
CCSD(T)/aug-cc-pV5Z	1.4973
Experiment[a]	1.4940

[a] Ref. [11].

Table 2 shows the ab initio energies and correction terms used in the present work. Values of $\Delta_f H_0$ (NS) derived via reaction (1) with different basis sets are plotted as a function of n for the cc-pV(n + d)Z series in Fig. 1. It may be seen that as $n \rightarrow \infty$, a limiting value is approached. We previously tested five fitting functions for extrapolation of energies to the CBS limit [20], and again for the present three working reactions we find that the best fit to the ab initio energies E is obtained with the three-parameter expression [29,30]

$$E(n) = E_{CBS} + b/(n + 0.5)^4 + c/(n + 0.5)^6. \quad (4)$$

Good performance was also shown by a simple exponential fit and a function proposed by Wilson and Dunning for extrapolation of MP2 energies [31]. For reaction (1), the CBS limit for $\Delta_f H_0$ (NS) is 276.3 kJ mol^{-1}. There are significant changes in the bonding and electronic structure of the atoms in this dissociation reaction, which are minimized in the congeneric reactions [32] (2) and (3) which exchange atoms from same chemical group. Errors in the computed reaction enthalpies are expected to cancel to some extent, and this is borne out by Fig. 1, which shows a much weaker dependence on the size of the basis set for these two processes. The extrapolations are therefore more certain, and results are close to the limit by the time $n = 4$. The CBS limits derived via reactions (2) and (3) are 276.7 and 277.8 kJ mol^{-1}, respectively. Our best estimate of $\Delta_f H_0$(NS) is the mean of these two

Table 2
Ab initio energies and correction terms[a]

Basis set	NS	N	S	NO	O_2	SO	H_2S	H_2O
CCSD(T)/aug-cc-pVDZ	−452.24265	−54.48686	−397.61053	−129.62566	−150.02105	−472.70305	−398.88085	−76.27390
CCSD(T)/aug-cc-pVTZ	−452.33875	−54.51673	−397.65611	−129.72677	−150.14114	−472.82221	−398.94083	−76.34233
CCSD(T)/aug-cc-pVQZ	−452.36764	−54.52532	−397.66795	−129.75870	−150.17880	−472.85770	−398.95731	−76.36359
CCSD(T)/aug-cc-pV5Z	−452.37872	−54.52803	−397.67181	−129.76897	−150.19115	−472.87094	−398.96319	−76.37030
CCSD(T)/aug-cc-pV(D + d)Z	−452.25260	−54.48686	−397.61451	−129.62566	−150.02105	−472.71354	−398.88793	−76.27390
CCSD(T)/aug-cc-pV(T + d)Z	−452.34321	−54.51673	−397.65724	−129.72677	−150.14114	−472.82736	−398.94361	−76.34233
CCSD(T)/aug-cc-pV(Q + d)Z	−452.37029	−54.52532	−397.66866	−129.75870	−150.17880	−472.86070	−398.95899	−76.36359
CCSD(T)/aug-cc-pV(5 + d)Z	−452.37903	−54.52803	−397.67214	−129.76897	−150.19115	−472.87174	−398.96371	−76.37030
Scalar relativistic correction	−1.10631	−0.02923	−1.07740	−0.08105	−0.10400	−1.12905	−1.07692	−0.05180
CCSD(T) = FULL/aug-cc-pwCVQZ	−452.79491	−54.57977	−398.04162	−129.86418	−150.28527	−473.28593	−399.33190	−76.41703
CCSD(T)/aug-cc-pwCVQZ	−452.36570	−54.52403	−397.66905	−129.74906	−150.16741	−472.85384	−398.95877	−76.35772
Spin–orbit correction	0.00050	0	0.00089	0.00027	0	0	0	0
Zero-point energy	0.00277	0	0	0.00432	0.00359	0.00261	0.01498	0.02110

[a] In au. 1 au = 2625.5 kJ mol^{-1}.

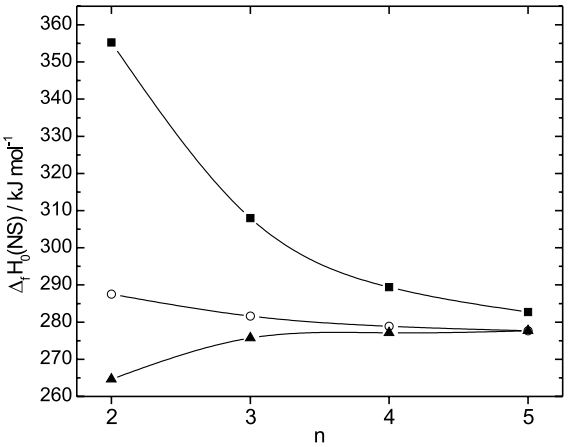

Fig. 1. Plot of the enthalpy of formation of NS derived with aug–cc–pV(n + d)Z basis sets. Three working reactions were employed: solid squares, NS → N + S; open circles, NS+ H_2O → NO + H_2S, solid triangles, NS + O_2 → NO + SO. The curves show fits (Eq. (4) in the text) which were extrapolated to the complete basis set limit.

values, 277.3 kJ mol^{-1}. As discussed in our previous work [20], the main sources of uncertainty are the basis set extrapolations and the scalar relativistic corrections, and here we conservatively allow for ±2 kJ mol^{-1} error limits.

Dunning et al. [24] recommend their cc-pV(n + d)Z basis sets over cc-pVnZ for improved convergence in species with second-row atoms. This is borne out in the present reactions. Initial attempts to derive CBS limits with the aug-cc-pVnZ basis sets led to CBS limits for $\Delta_f H_0$ from reactions (1)–(3) of 268, 261 and 279 kJ mol^{-1}, respectively. The convergence was slower than with the extra d functions, and as a consequence, the CBS values are more scattered and not used in this work. Our value for $\Delta_f H_0$ (NS) is consistent with the limited experimental data discussed in Section 1, and the calculation by Nguyen and coworkers [16], but has a much smaller uncertainty. Thermal corrections yield $H_{298} - H_0 =$ 9.40 kJ mol^{-1} and hence $\Delta_f H_{298}(\mathrm{NS}) = 278.0$ kJ mol^{-1}.

The implied N–S bond dissociation enthalpies at 0 and 298 K, respectively, are 468.2 and 471.7 kJ mol^{-1}. The former value compares well with O'Hare's [12] value of 463 ± 24 kJ mol^{-1}, but with much smaller uncertainty. Gaydon [33] con-

sidered linear Birge–Sponer extrapolations of 589 and 550 kJ mol^{-1}, and recommended 482 ± 68 kJ mol^{-1}, which encompasses our calculated value.

D_0(S–O) is 516.5 kJ mol^{-1} [14], so it may be seen that sulfur bonding to nitrogen is somewhat weaker than to oxygen. We might therefore expect NS to be labile in an oxidizing environment. Direct oxidation of NH_2 by O_2 is extremely slow [34], but in the presence of sulfur, NH_2 may be converted to NS which could provide an alternative route to NO_x. Our thermochemistry together with JANAF data [14] indicate that

$$NH_2 + SO \rightarrow NS + H_2O \quad (5)$$

is exothermic by 159 kJ mol^{-1} and is therefore feasible. Schofield considered

$$NS + OH \rightarrow NO + SH \quad (6)$$

to be a potential fate of NS and source of NO_x [35], and the present thermochemistry shows that reaction (6) is exothermic by 87 kJ mol^{-1} at 298 K.

4. Conclusions

Coupled-cluster calculations, together with extrapolation to the complete basis set limit and corrections for anharmonic zero-point energy, relativistic terms and core–valence electron correlation, yield an enthalpy of formation of NS that should be reliable to within about 2 kJ mol^{-1}.

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